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# The Raman Effect of Cis and Trans-Decalin

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## Abstract

Several of the physical properties of liquid cis-decalin seem to change at about 55°C. The surface tension-temperature curve for example shows a change in slope at about this temperature. It was thought of interest to study the Raman effect of the two isomers as a function of temperature in order to find out if the scattering power of the two isomers shows different behavior over the temperature range 25°-75°C. It appears that the scattering of trans-decalin remains about the same over this temperature range while the cis-isomer shows increased scattering at the higher temperature. Some ideas are expressed that might account for the phenomenon.


## Introduction

Decalin can be prepared by the reduction of naphthalene and a mixture of two isomers, cis- and trans-decalin results. These isomers can be separated by fractional distillation at reduced pressure (10 mm) and they can be further purified by crystallization (1). The structure of these isomers has been determined by electron diffraction by Bastiansen and Hassel (2). This model of cis-decalin differs from the one originally suggested by Sachse (3) and Mohr (4). The trans-decalin configuration is the usual one given by the earlier investigators. Barton (5) favors the cis-decalin model proposed by Bastiansen and Hassel on the basis of some energy considerations concerned with the interaction of non-bonded atoms.

## Physical Properties

Seyer and his coworkers (6-9) studied the physical properties of the two isomers mentioned above and they found that the properties of trans-decalin showed a nearly linear relationship with temperature. However the similar properties for cis-decalin indicated some irregularities such as a change in slope of a graph of the property with temperature. These changes happen at about 55°C. According to Seyer and Davenport (6) the density-temperature and the refractive index-temperature curves of both isomers are nearly linear and practically parallel over the temperature range studied (0-140°C). The surface tension-temperature curves of both isomers are not quite straight lines in this temperature interval. While the trans-decalin curve shows a smooth change of slope, the corres-

ponding graph for cis-decalin appears to have a rather abrupt change in slope at about 50°C (6). Viscosity measurements (in the range −30 to 180°C) as studied by Seyer and Leslie (7) when plotted as log $\eta$ as a function of 1/T are not quite linear, but they are quite smooth and there appears to be no evidence to support the discontinuity found with surface tension at 50°C for the cis-isomer. However in the case of cis-decalin a slight deviation in the slope seems noticeable at 110° and it increased with higher temperatures. Furthermore the longer the hydrocarbon was kept at any one temperature in this interval, the greater became its viscocity. The authors suggest molecular association as a possible cause for this behavior. In reference to vapor pressure it was found by Seyer and Mann (8) that these two liquids behave somewhat abnormally with respect to changes in temperature. The usual log P vs 1/T curves are approximately linear only at the higher temperatures (60-227°C). At lower temperatures (−23 to 60°C) both curves show decided curvature and the cis-decalin curve has the greater change in slope. The specific heat of cis-decalin shows peculiar behavior at about 50°C and is interpreted by Seyer as an indication of a second order phase change at that temperature (9).

## Raman Effect

It was thought that a study of the Raman effect of the two isomers might give some information regarding this marked difference in their behavior. The Raman effect had been observed by earlier investigators. Fifty-two Raman lines were obtained by Mitra (10) who also noted a region of continuous scattering between 2849 and 2923 A. Saskena (11) separated the Raman lines of cis- and trans-decalin and Inamura (12) states that the cis-isomer has the chair-form while the trans-form is gauche, based on his studies of the Raman effect. None of these workers experimented over a temperature range. In the present investigation the Raman effect was studied at 25, 57 and 75°C. The experimental arrangement permitted the observation of the light scattering of both isomers at the same time. Two identical Raman tubes were placed into the light furnace so that any fluctuations in light intensity and temperature would affect both liquids equally. The apparatus was tested with carbon tetrachloride and has already been described (13). In the latter case both Raman tubes contained carbon tetrachloride and both tubes were wrapped in polaroid sheets. However the directions of the electric vectors were different by ninety degrees in the two tubes. Very satisfactory pictures for carbon tetrachloride were obtained with this arrangement (14).

The light scattering obtained with this two Raman-tube-apparatus for cis- and trans-decalin showed that the scattering intensity of trans-decalin is the same at 25° as at 50°C. However cis-decalin exhibited a distinct difference in scattering intensity at these two temperatures. It scatters light much better at room temperature than at 57 or 75°C (Fig. 1). Hence these experiments also indicate that cis-decalin behaves differently from trans-decalin when it is heated to about 55°C or above.

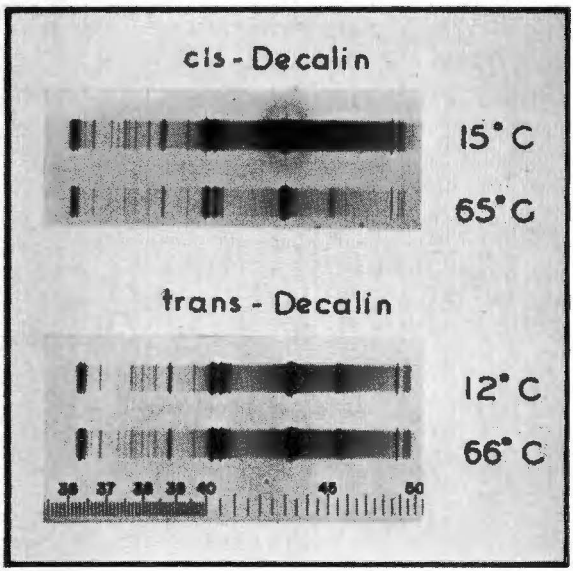


Figure 1. Raman Scattering of Cis- and Trans-Decalin.

## Discussion

The behavior of cis-decalin in the temperature range around 50°C is very remarkable and it is natural to inquire what type of phenomenon could be taking place to cause a change in surface tension, the refractive index, the specific heat of the substance and its light scattering power. The change in specific heat seems to indicate a possible transition point. It cannot be a first order transition such as melting and evaporation since only one liquid phase is present. The following five possibilities can be considered:

1. A second-order phase transition. 2. A change in vibrational quantum states. 3. Isomeric structure transition. 4. Chemical change. 5. Coacervation. These effects were considered elsewhere (13) in detail and the only phenomenon which seems to account for the relatively sharp transition at about 50°C is coacervation. The

other possibilities mentioned are expected to show a relatively gradual change with temperature. It is conceivable that the liquid exists in a cybotactic state below 50°C and that this state goes over into a more disordered condition rather rapidly as the temperature reaches a critical value. The more orderly arrangement of the islands or swarms of molecules may possibly change to the more normal liquid condition at about 50°C. The case here considered is different from simple association. The size of the swarms of molecules would very likely contribute to the greater scattering power of the liquid at the lower temperature. This idea could be tested by studying the X-ray scattering of cis-decalin. Furthermore it seems necessary that all the properties of cis-decalin be re-examined.

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